Supporting Information for

Size-Controlled Synthesis and Morphology-Evolution of Bismuth Trifluoride Nanocrystals via a Novel Solvent Extraction Route

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Experimental Section

Materials:

Acid-base-coupled extractant (PN) was obtained through the reaction of equal mols of the commercial extractants PC-88A and N1923. PC-88A (purity > 95%) and N1923 (purity > 99%) were kindly supplied by Shanghai Organic Chemistry Institute (Chinese Academy of Sciences), and they were used without further purification. Organophosphorus acid, PC-88A, the effective component of which is 2-ethylhexyl 2-ethylhexyl-phosphonic acid, is an excellent reagent for the solvent extraction of various metals. Secondary carbon primary amine N1923, with two straight chain alkyls and an average molecular weight of 280.69, can extract mineral acid and solubilize water.

Synthesis of Bismuth Trifluoride Nanocrystals:

Prepared PN in heptane (16%) is used to extract Bi^{3+} and hydrofluoric acid, respectively. Then the organic phases loaded with Bi^{3+} (PN-Bi) and HF (PN-HF) are used as the metal and fluorine sources for the formation of BiF_3 nanocrystals, respectively. In a typical synthesis of BiF_3 hexagonal nanoplates, 30 mL of PN-Bi containing 0.04 M Bi^{3+} and 6.1 mL of PN-HF containing 0.59 M HF are mixed together in an air atmosphere at room temperature according to a Bi/F molar ratio of 1:3 and the reaction is maintained for 1 h. Then the products are collected at the bottom of the vessel, after which the extractant PN can easily be recycled from the mother liquid after purifying with hydrochloric acid and water. Pure powders can be obtained by washing the samples with acetone or ethanol several times to remove the extractant. Finally, the product is dried in an oven at 60°C for 5 h and 300 mg of nanoparticles can be obtained, according to a yield of 94% based on the theoretical amount of 319 mg. The reaction can also be readily scaled up to meet the demand for the preparation of a larger amount of product. The reaction conditions can also be changed to prepare BiF_3 nanocrystals of other shapes.

Structure Characterizations:

The structures of the materials were characterized with an X'Pert Pro MPD X-ray diffractometer (Philips, The Netherlands) using Cu Kα radiation (1.5405 Å). The morphologies of the materials were observed with a scanning electron microscope (Hitachi S-4800) and a transmission electron microscope (JEOL 2010). The Brunauer-Emmett-Teller (BET) surface area was deduced from an isotherm analysis.

Fourier transform infrared spectroscopy (FTIR) measurements were performed on a Bruker Tensor 27 Spectrometer using KBr pellets (32 scans at a resolution of 4 cm^{-1}) in transmission mode. An acid-base titration method using standard NaOH solution was used to determine the HF concentration in the reversed micelle systems. A complexometric titration method with standard EDTA solution was used to determine the Bi^{3+} concentration in the bottom aqueous phase. The concentrations of Bi^{3+} in the upper organic phases were determined by difference.

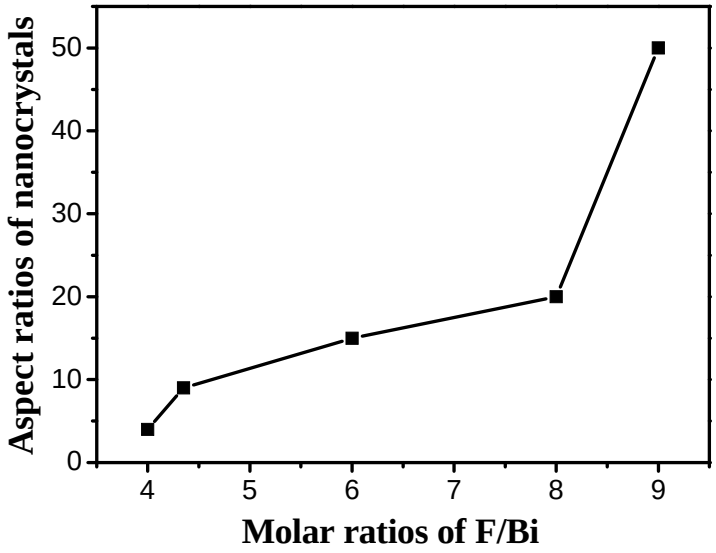

Figure S1. The relationship between aspect ratio of obtained nanocrystals and molar ratio of F:Bi in precursors.

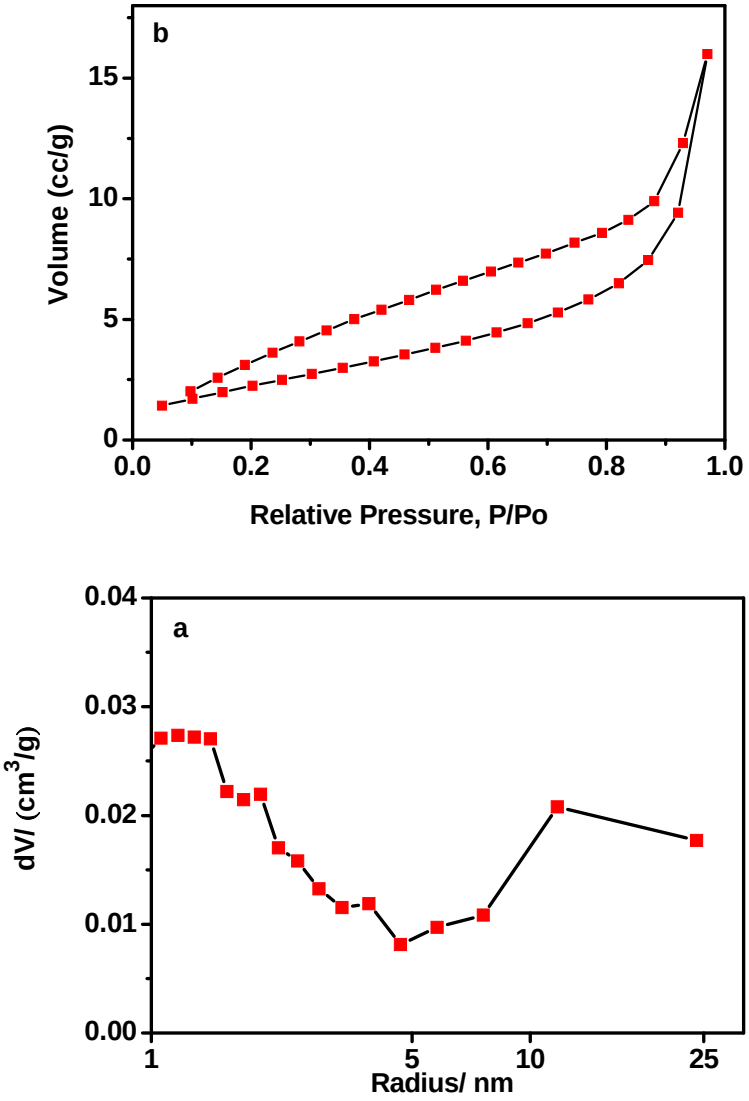

Figure S2. a) Typical nitrogen adsorption/desorption isotherms of the as-synthesized BiF_3; b) Pore diameter distribution plot for the as-synthesized BiF_3.

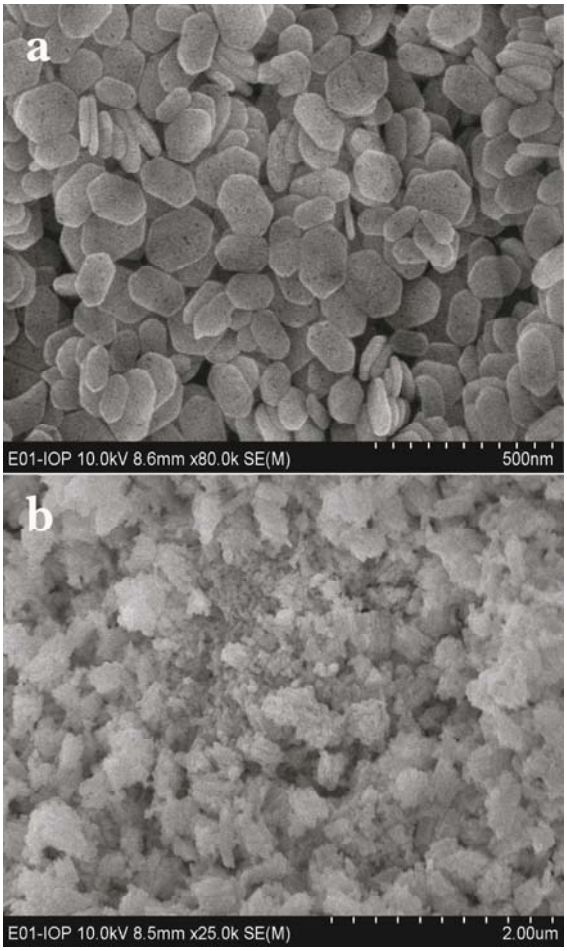

Figure S3. SEM images of hexagonal nanoplate BiF_3 before (a) and after calcination (b) at 300°C for 2 h.

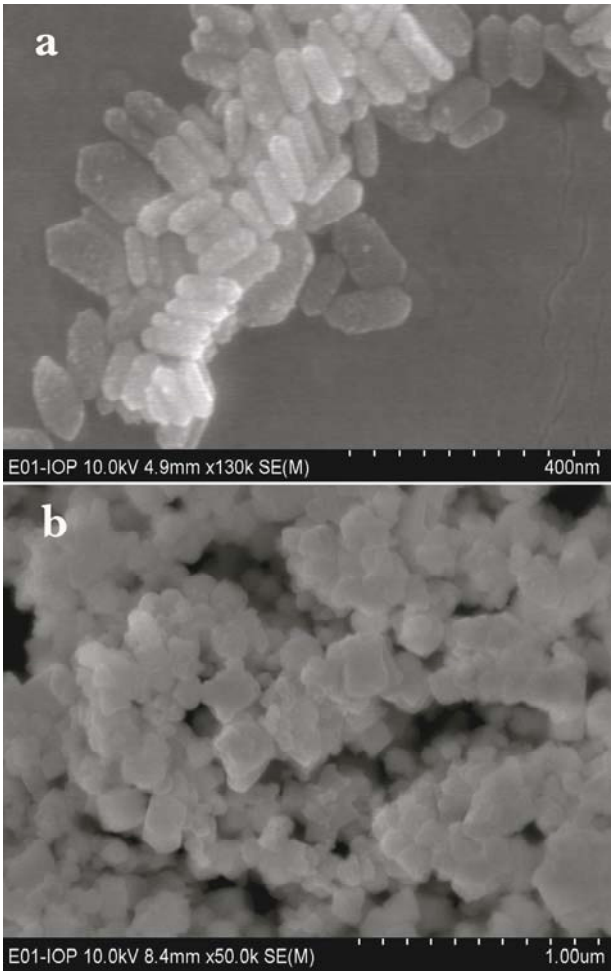

Figure S4. SEM image of the as-prepared BiF_3 sample washed only by acetone or ethanol (a). SEM image of the same sample washed by acetone or ethanol together with water (b).

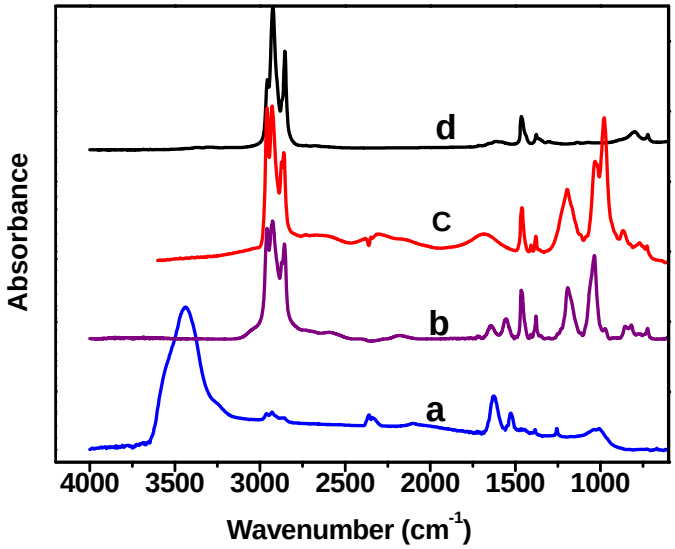

Figure S5. FTIR spectra for a) as-synthesized BiF_3 powder, b) pure PN, c) pure PC-88A and d) pure N1923.

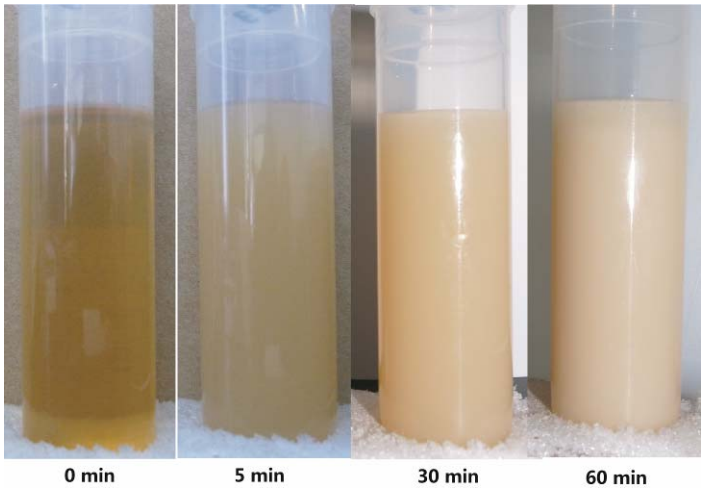

Figure S6. Digital photos for the formation of precipitation at different reaction times.